

AD-A225 269

WRDC-TR-90-2024



KINETICS OF ORGANOPHOSPHATE REACTIONS

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April 1990

Final Report for Period of June 1987 - June 1989



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REPORT DOCUMENTATION PAGE

Form Approved
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1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS N/A		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release distribution is unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A			5. MONITORING ORGANIZATION REPORT NUMBER(S) WRDC-TR-90-2024		
6a. NAME OF PERFORMING ORGANIZATION University of Pittsburgh Dept. of Physics & Astronomy		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION WRDC/POOC-3		
6c. ADDRESS (City, State, and ZIP Code) Pittsburgh, PA 15260			7b. ADDRESS (City, State, and ZIP Code) Wright-Patterson AFB, OH 45433-6563		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Advanced Plasma Research Group		8b. OFFICE SYMBOL (If applicable) POOC-3	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F3361587C2754		
8c. ADDRESS (City, State, and ZIP Code) Wright Research and Development Center Wright-Patterson AFB Ohio 45433-6563			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2301	TASK NO. S1
11. TITLE (Include Security Classification) KINETICS OF ORGANOPHOSPHATE REACTIONS					
12. PERSONAL AUTHOR(S) Rainer Johnsen					
13a. TYPE OF REPORT FINAL		13b. TIME COVERED FROM 87/6 TO 89/6		14. DATE OF REPORT (Year, Month, Day) 90 04 19	
15. PAGE COUNT 26					
15. SUPPLEMENTARY NOTATION					
17. COSATI CODES			19. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Dimethyl Methylphosphonate, Ion Molecule Reactions		
FIELD	GROUP	SUB-GROUP			
15	2	3			
15	2	5			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Rate coefficients and product-ion yields have been determined for ion-molecule reactions of several atmospheric ions with dimethyl-methylphosphonate (DMMP). The measurements were carried out using a selected-ion drift-tube mass spectrometer. Most reactions are found to proceed by dissociative charge transfer. Those of nitric oxide ions in the electronic ground state occur by three-body association, those of hydronium ions occur by proton transfer.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL MAJOR THOMAS E. GIST			22b. TELEPHONE (Include Area Code) (513) 255-2923		22c. OFFICE SYMBOL WRDC-POOC-3

Preface

This work was performed in the laboratories of the Department of Physics and Astronomy of the University of Pittsburgh. The work was performed under Contract F33615-87-C-2754 with the United States Air Force through the Wright Research and Development Center.

The authors acknowledge helpful discussion with Dr. P. Chantry of Westinghouse Corporation and Dr. S. Dheandhanoo of Extrel Inc.

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Section I

Introduction

In order to provide rate constant data for model calculations of electrical discharges containing air and DMMP vapor, we have performed a series of measurements on the reactivity of selected atmospheric ions with dimethyl-methylphosphonate (DMMP) in the ion-energy range from thermal (0.04 eV) to about 1 eV. The experiments were carried out in a selected-ion drift-tube mass spectrometer apparatus. The results of this work include rate coefficients, product-ion yields, and the variation of these quantities with ion energy. Wherever possible, we have attempted to ascertain the electronic state of the reacting ions and to determine the reactivity of electronically excited ions separately.

After a brief description of the experimental techniques and a review of known physical and chemical properties of DMMP, we will present the results and will discuss possible reaction mechanisms.

Section IIa

Experimental Methods

The experimental apparatus used in this work was the selected-ion drift tube mass-spectrometer that has been described in detail earlier [1]. The only modification required for the present work was the addition of a gas inlet to admit DMMP vapor.

In this apparatus (see Fig. 1), parent ions are produced by an electron-impact ion source and are passed through a quadrupole mass filter to select only those ions of the desired charge-to-mass ratio, e.g., to separate atomic and molecular oxygen ions.

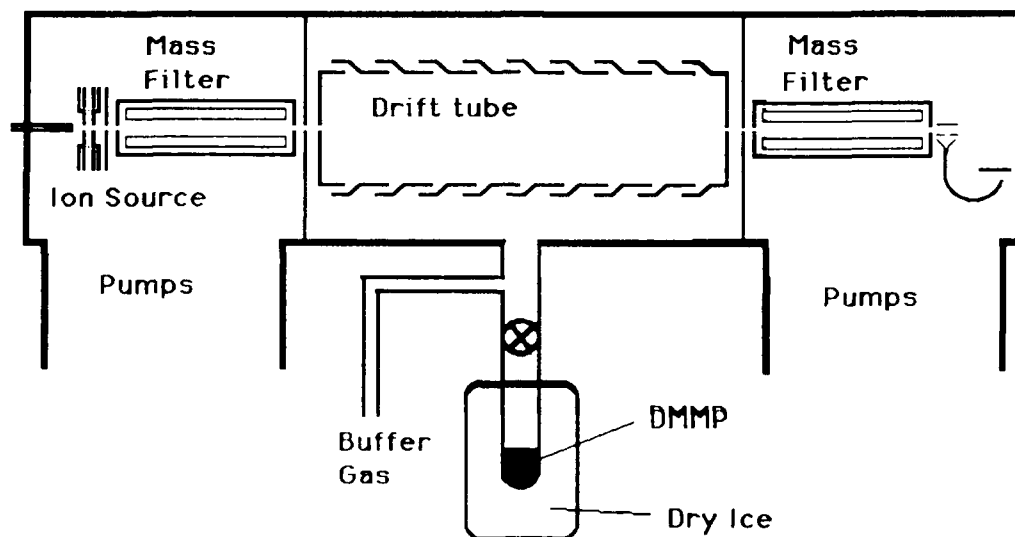


Fig. 1 Diagram of the selected -ion drift tube apparatus and DMMP inlet system.

The ion source can be operated in a pulsed mode (producing ion pulses of 5 to 10 μsec , repeated at typically 1 msec intervals) or in the continuous mode. The selected ion species is injected into the drift/reaction region which contains helium buffer gas at pressures from 0.5 to 1 Torr and DMMP vapor at pressures from 0.01 to 0.1 mTorr. The drift region has a length of 36 cm, the axial drift field ranges from 0 to 10V/cm. A second mass spectrometer analyzes the ions effusing from the drift tube through a small

sampling orifice. The mass resolution of the analyzer is adjustable from very low ($m/Dm < 20$) to high ($m/Dm > 500$) values. Ions are detected by a particle multiplier and ion counts are accumulated in a multichannel analyzer.

To obtain total rate coefficients, the additional residence time technique [2] is used, i.e., the electric drift field is either electronically switched off (for thermal-energy measurements) or it is reversed (for above-thermal-energy measurements) during a short time interval Δt . In this manner, the ions' residence time in the drift tube can be varied and the concentration of ions can be measured as a function of residence time. Rate coefficients are then obtained from the observed loss rate of parent ions after a correction for diffusive losses is applied to the data. The loss of ions, owing to diffusion, is obtained by repeating the same experiment in pure buffer gas. Since the partial pressure of the reactant is only a small fraction of the total pressure, the diffusive losses in the gas mixture are nearly identical to those in the pure buffer gas.

The mean ion energy of ions drifting in a gas (in the laboratory frame) is related to the ions' drift velocity by the formula given by Wannier [3]

$$\langle e_{ion} \rangle = 3/2 kT + (m + M) v_d^2 / 2 \quad (1)$$

where m and M are the masses of the ion and buffer gas atoms, respectively, and v_d is the ions' drift velocity. We have used our measured values of the parent ions' drift velocity to calculate $\langle e_{ion} \rangle$ and the corresponding energy in the center-of-mass of the ion-reactant system. The mean ion energy relaxes very quickly after reversal or interruption of the drift field. Relaxation times have been estimated by Johnsen and Biondi [4] from momentum-loss frequencies and by Lin et. al. [5] using both analytical and Monte Carlo methods. Relaxation time constants are typically less than 1 msec for the parent ions used in this work while residence times are typically 100 to 1000 msec.

The distribution of ion energies is precisely maxwellian in the field-free measurements at thermal energies. At the highest ion energies (~ 1 eV), the energy distribution functions are not maxwellian; the spread of ion energies about the mean is then approximately given by $\langle e_{ion} \rangle [m/(M+m)]$, where $m = 4$ (mass of helium) and M is the mass of the parent ion in atomic mass units.

The determination of product-ion yields was carried out in several steps. After taking initial, low-resolution mass scans to identify likely products, high-resolution mass scans were obtained to ensure that an observed product ion mass peak contained only ions of a single mass-to-charge ratio. In a second step, the arrival time spectra of both parent and product ions were recorded to verify, by inspection of their time correlations, that an observed ion species was produced by the parent ion under study, rather than by extraneous reactions. Subsequently, the analyzer mass filter was set to lower mass resolution to obtain minimal mass discrimination, and product-ion mass spectra were recorded to obtain relative product-ion yields. All product peaks were recorded. Yields are calculated by dividing the intensity for a given ion by the sum of the intensities of all ions. In the last step, the ion source was operated in the continuous mode to take advantage of the higher attainable ion currents. All measurements of product ion yields were made at very low DMMP concentrations (less than 1 mTorr) to eliminate secondary ion-molecule reactions of the primary product ions with DMMP. The density of ions in the drift tube is typically on the order of 10^5 cm^{-3} , i.e. it is very small compared to neutral densities. The presence of ions has essentially no effect on the electric field in the drift tube.

DMMP vapor was obtained from liquid DMMP samples contained in a glass bulb that was kept at temperatures near that of dry ice; a thermocouple with digital readout monitored the actual temperature. The DMMP vapor pressure in the drift tube was measured with a capacitance manometer (MKS Baratron). Readings of the DMMP pressure (in the absence of the buffer gas) were taken before and after each measurement and, if the two readings differed, they were interpolated to obtain the value at the time the data were taken. The DMMP reservoir was connected to the drift tube by a short (10 cm) and wide (2.5 cm in diameter) piece of tubing in order to avoid diffusive density gradients between the DMMP reservoir and the drift tube, which would otherwise arise after addition of the helium buffer gas. Even with these precautions, the uncertainty in the DMMP concentration (estimated to be about 10 %) was the principal source of error affecting the rate coefficients. Fresh DMMP samples (obtained from Aldrich Chemical Inc.) apparently contained some impurities, dissolved atmospheric gases and possibly methanol. Prolonged and repeated pumping on the samples reduced these impurities to tolerable levels. Further purification by distillation and discarding part of the distillate did not give better results than prolonged pumping.

Section II b

Physical and Chemical Data of DMMP

DMMP, $(\text{CH}_3 \text{O})_2 \text{CH}_3 \text{PO}$, is liquid at room temperature. Its vapor pressure at room temperature is approximately 1 Torr ; at low temperatures (near dry ice temperature), the vapor pressure was measured to vary as shown in Fig. 2.

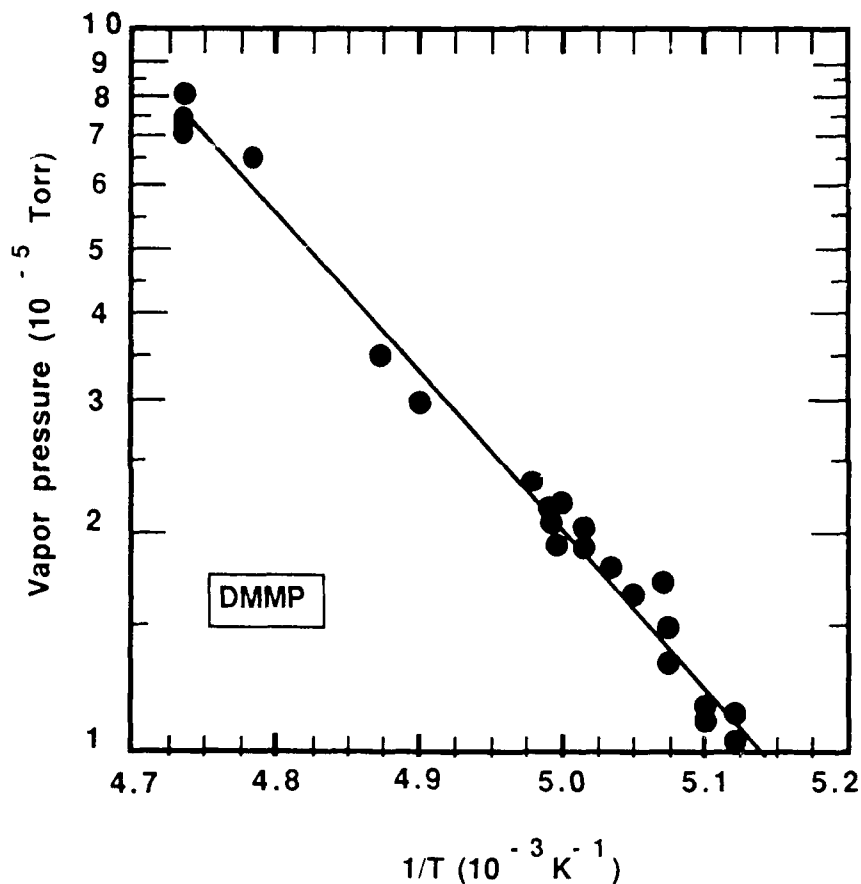


Fig.2 Semi-logarithmic graph of measured vapor pressures of DMMP as a function of the reciprocal temperature in Kelvin. The line corresponds to the functional dependence given in the text.

We include this figure here, since such data are not available in the literature. The variation of the vapor pressure in this temperature range is well described by an expression of the form $p \text{ (Torr)} = 3.76 \times 10^6 \exp (-5190/T [\text{K}])$. The vapor pressure curve

was used to determine the temperature needed for a desired DMMP pressure and to judge the precision to which the temperature of the DMMP reservoir needed to be stable during an experimental run.

The ionization potential of DMMP has been measured to have a value of 10.48 eV [6]; its proton affinity has been given as 9.7 eV [7].

Section III

Experimental Results

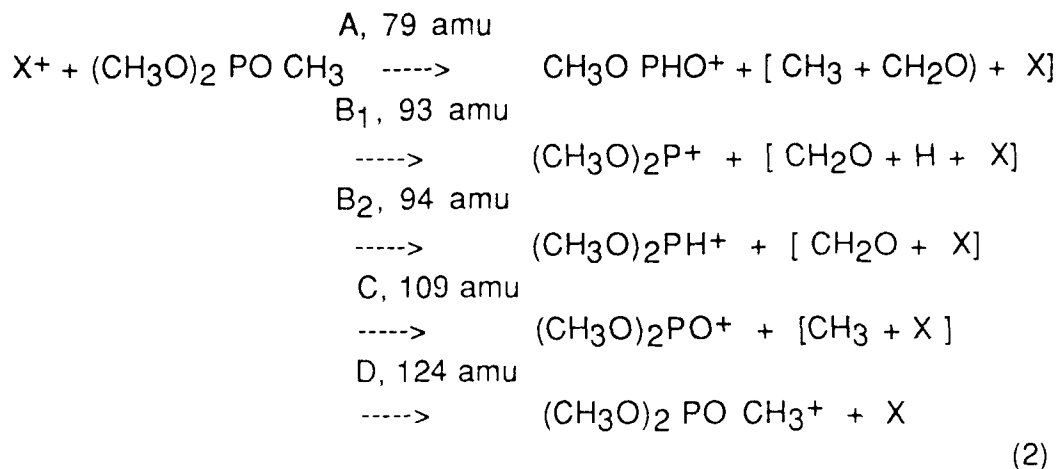
In the following sections we will present our experimental observations and will give the results for reactions of different parent ions. A compilation of rate coefficients and product-ion yields at thermal energy also appears in Table I.

Uncertainties in the total rate coefficients are expected to be less than 10 %. The largest source of error arises in the determination of the DMMP vapor density. The influence of possible mass-discrimination effects on the measured relative abundances of product ions was considered. To reduce such effects in the ion analyzer and detection system, the mass filter was operated at low resolution where the transmission is independent of mass. After transmission through the quadrupole, the ions were accelerated to the 3kV potential of the ion-detector's cathode. It seems unlikely that the detection efficiency of energetic ions would depend much on their mass or chemical nature.

More important discrimination effects may arise in the drift tube itself since ions of different mass suffer different lateral (transverse to the applied electric field) diffusion losses. We estimated the magnitude of such effects by using the expressions for lateral diffusion coefficients of drifting ions given by Mason and McDaniel [8]. The effects are absent in the limit of $E/N = 0$ as a result of Einstein's relation between mobility and diffusion ($D = m kT/e$), since in that limiting case the product $D\tau t$ ($D\tau$ being the lateral diffusion constant, and t being the time between creation and detection of an ion) is the same for all ions. At high values of E/N , different ions may acquire different mean energies, so that their lateral diffusion losses become unequal. Under the conditions of our experiments the effect is rather small, largely because the ions are far heavier than helium atoms and their reduced mass with helium is nearly the same for all product ions. We estimate that, at the highest values of E/N , diffusion would cause a <5% reduction of the product-ion signal of the lightest

ion (79 amu) relative to that of the heaviest ion (124 amu). No correction was applied to the data. These errors should be far smaller at lower fields.

The reactions of O^+ , O_2^+ , N^+ , and N_2^+ ions with DMMP were found to have very similar product ions. If we denote any of these ions by X^+ , the reactions take the form



We have labelled the branches A, B_1 , B_2 , C, D in order of ascending product-ion masses. There is an ambiguity in inferring the chemical formula of the product ions in branches A and B_1 from the observed mass-to-charge ratio. For instance, PO_3^+ also has a mass of 79 amu and $PO_3CH_3^+$ also has a mass of 94 amu. Since our mass spectrometers have insufficient resolution to separate close mass doublets, we have based the identification of the ions on the electron impact ionization studies of DMMP by Bafus et al. [6]. The high-resolution mass spectra obtained by those authors indicate that dissociative ionization produces the ions indicated in Eq. 2, rather than the alternatives given above.

It was not possible to set the resolution of the mass spectrometer so that the branches B_1 and B_2 were well resolved without causing at the same time mass discrimination relative to other ions. To circumvent this problem, we first determined the sum of branches B_1 and B_2 and compared it to the intensities of the other product ions. In a second step, the mass spectrometer was set to resolve B_1 and B_2 and the variation of their relative abundance with ion energy was measured.

As a by-product of this work, we obtained reasonably accurate (uncertainties of about 5 %) values for the ionic mobilities of the ions A, B₂, C, D in helium. The reduced mobilities m_0 (i.e., those reduced to a standard gas density of $2.69 \times 10^{19} \text{ cm}^{-3}$) were:

CH ₃ O PHO ⁺ in helium:	$m_0 = 14.1$	cm ² /Vs
(CH ₃ O) ₂ PH ⁺ in helium:	$m_0 = 12.4$	cm ² /Vs
(CH ₃ O) ₂ PO ⁺ in helium:	$m_0 = 12.2$	cm ² /Vs
(CH ₃ O) ₂ PO CH ₃ ⁺ in helium:	$m_0 = 11.2$	cm ² /Vs

Section IV

Results for Particular Reactions

To facilitate presentation of measured results, all numerical data have been compiled in Table 1. Graphs of measured rate coefficients and product-ion abundances as a function of energy are given in the sections for particular parent ions. Random errors in these quantities are typically on the order of +/-10 %, unless otherwise stated.

Section IV A

Reactions of O⁺ and O₂⁺

Total rate coefficients for the reactions of O⁺ and O₂⁺ ions with DMMP were measured as a function of ion energy from 0.04 to 0.7 eV and 0.04 to 0.9 eV (in the center-of-mass frame of the ion-reactant system). The reactions are fast ion-molecule reactions and, as is typical for fast reactions, there is essentially no variation of the rate coefficients with ion energy. Measured rate coefficients and product yields are given in Figures 3 through 6. In the graphs of product yields, the sum of branches B₁ and B₂ has been plotted since the two branches were not resolved in low-resolution mass spectra. The text should be consulted for statements concerning the relative importance of the two branches.

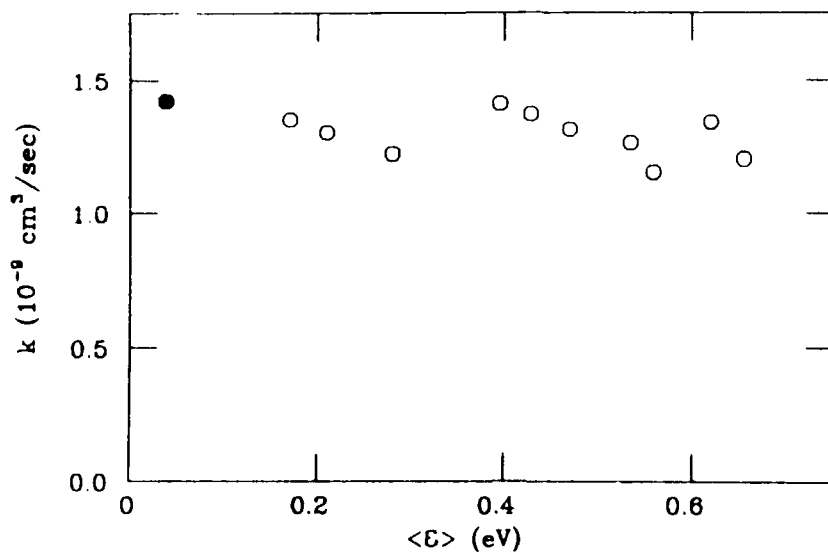


Fig. 3 Total rate coefficients for the reaction $\text{O}^+ + \text{DMMP}$ as a function of ion energy in the ion/reactant center-of-mass system.

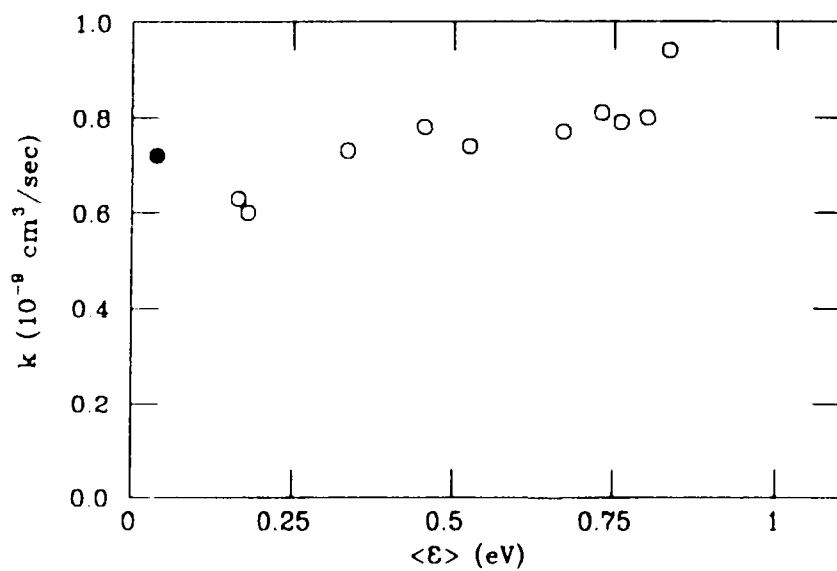


Fig. 4 Total rate coefficients for the reaction $\text{O}_2^+ + \text{DMMP}$ as a function of ion energy in the ion/reactant center-of-mass system.

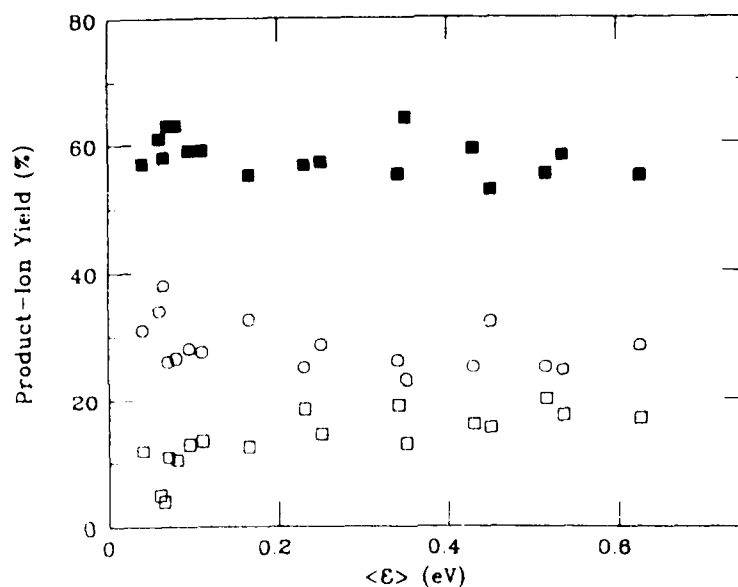


Fig. 5 Product-ion yields of the $O^+ + DMMP$ reaction as a function of ion energy in the ion/reactant center-of-mass system. Filled squares: Branch A. Open circles: Sum of B_1 and B_2 . Open squares: Branch C.

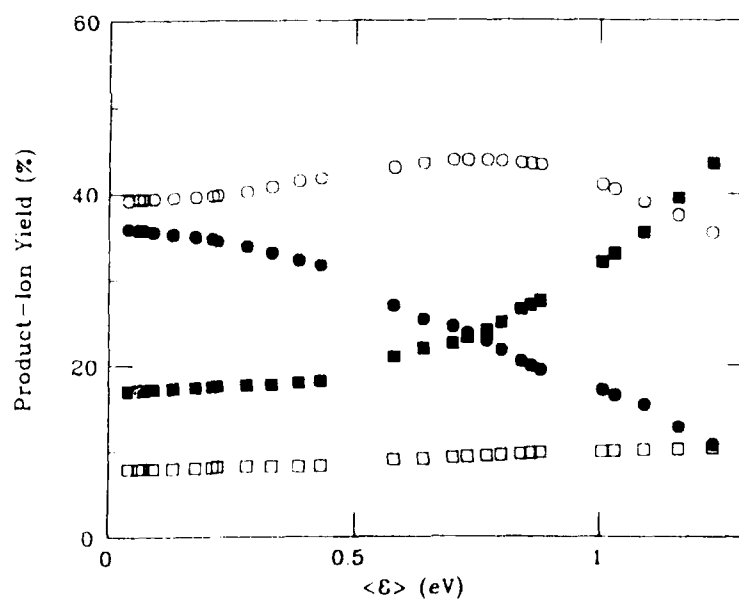


Fig. 6 Product-ion yields of the $O_2^+ + DMMP$ reaction as a function of ion energy in the ion/reactant center-of-mass system. Filled squares: Branch A. Open circles: Sum of B_1 and B_2 . Open squares: Branch C. Filled circles: Branch D.

The product-ion mass spectra indicated the existence of five reaction branches, those labelled A, B₁, B₂, C, and D in Eq. 2. In the case of the O₂⁺ + DMMP reaction, the product-ion abundances were found to vary strongly with ion energy, as shown in Fig. 2. No such variation of product-ion abundances was found in the O⁺ + DMMP reaction, except that the relative importance of channels B₁ and B₂, which differ by only one H atom, varied strongly with energy. Branch B₁, which was undetectably small in the reaction of O₂⁺, accounted for about 18 % of the sum of B₁ and B₂ in the O⁺ reaction at thermal energy, but increased to 66 % of the sum of B₁ and B₂ at the highest ion energy.

Both reactions refer to ions in the electronic ground state. It is known from past work [9] that metastable O⁺ 2D ions and metastable O₂⁺ (4p_u) ions have ionic mobilities that are slightly smaller than those of ground state ions. Thus, the presence of metastable oxygen ions is easily detected in drift tube experiments and ion source conditions were adjusted to obtain only ground-state ions.

Section IV B

Reactions of N⁺ and N₂⁺

The reactions of N⁺ and N₂⁺ were also found to be fast. Neither their total rate coefficients nor their product yields showed significant variations with ion energy as seen in Figures 7 through 10. However, branch D in the N₂⁺ reaction was found to decrease from an abundance of 10 % at thermal energy to less than 2% at 1 eV. In the N⁺ reaction, the branch labelled B₂ dominated over the branch B₁ in the ratio 2 to 1, independent of ion energy. In the reaction of N₂⁺, the B₂ channel was not observed.

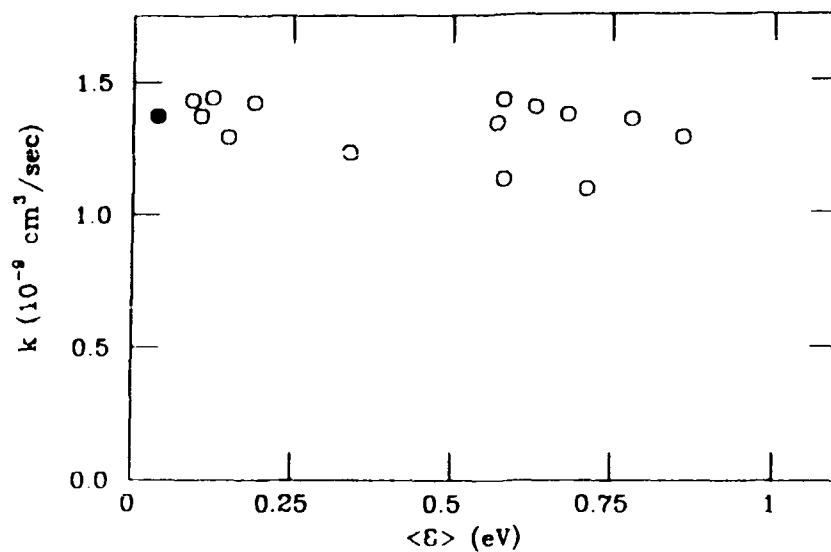


Fig. 7 Total rate coefficients for the reaction $\text{N}^+ + \text{DMMP}$ as a function of ion energy in the ion/reactant center-of-mass system

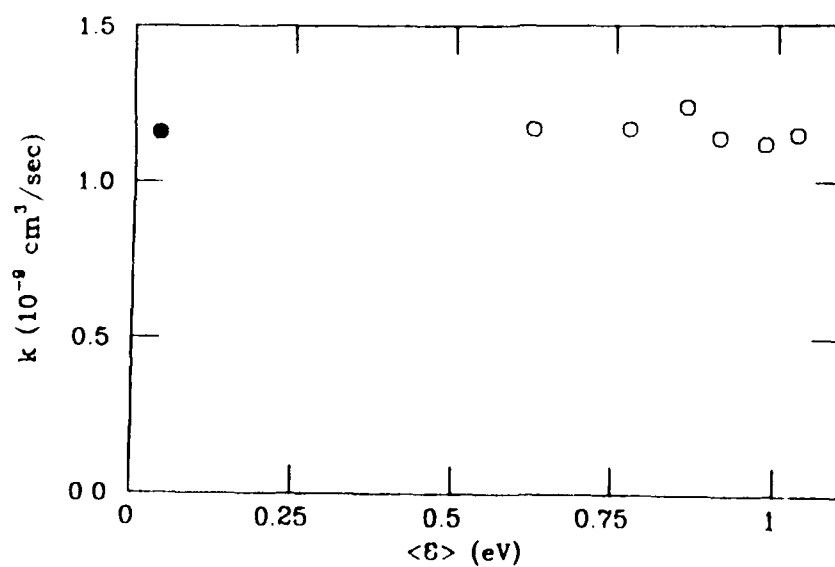


Fig. 8 Total rate coefficients for the reaction $\text{N}_2^+ + \text{DMMP}$ as a function of ion energy in the ion/reactant center-of-mass system.

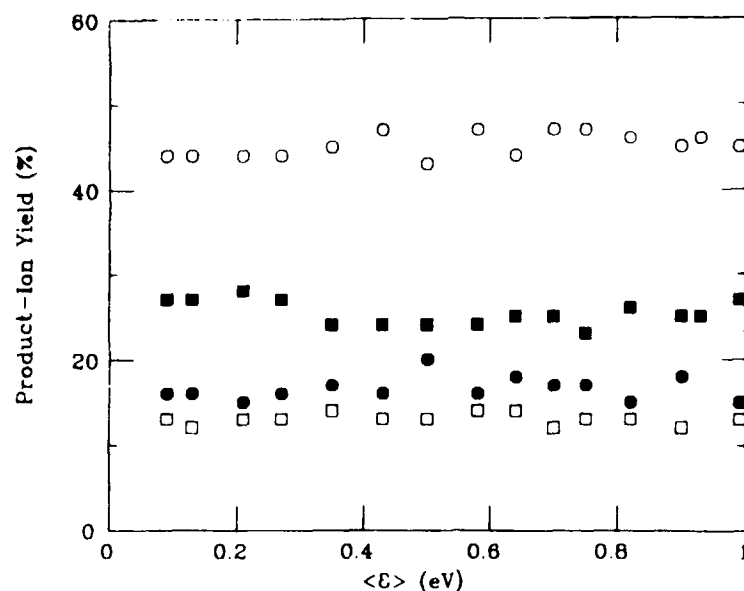


Fig. 9 Product-ion yields of the $N^+ + \text{DMMP}$ reaction as a function of ion energy in the ion/reactant center-of-mass system. Filled squares: Branch A. Open circles: Sum of B_1 and B_2 . Open squares: Branch C.

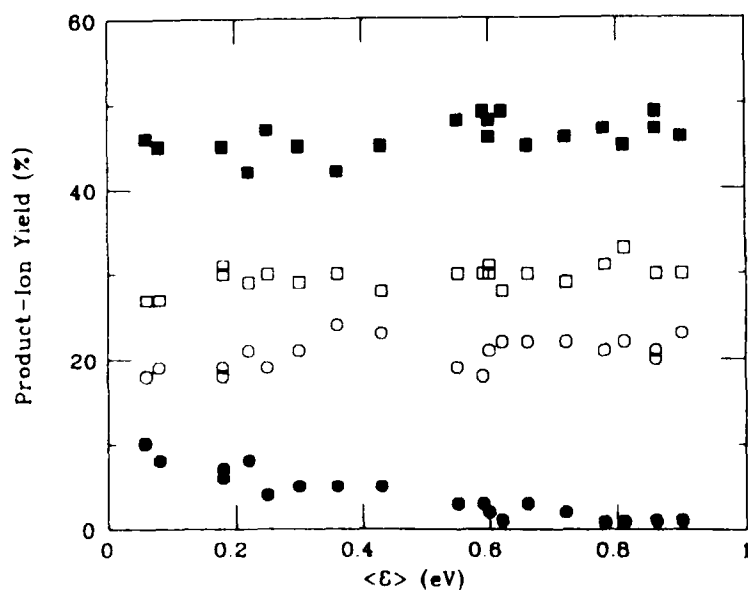
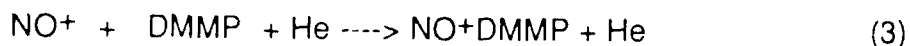


Fig.10 Product-ion yields of the $N_2^+ + \text{DMMP}$ reaction as a function of ion energy in the ion/reactant center-of-mass system. Filled squares: Branch A. Open circles: Branch B₁. Open squares: Branch C. Filled circles: Branch D.

Section IV C

Reactions of NO⁺

The experimental observations in the NO⁺ reactions with DMMP were initially somewhat confusing until we realized that the NO⁺ ions produced in the electron impact ion source contained a significant fraction of metastable NO⁺ ions in the a^3S^+ state, with an energy of 15.7 eV [10] above the NO ground state. We know that these metastable ions react with argon by charge transfer and that they are quenched to the electronic ground state by collisions with neutral nitric oxide [11]. After addition of either gas to the drift tube, the metastable fraction of the ions was removed and the only significant product ions were NO⁺ ions clustered to DMMP. These ions apparently were formed in the three-body association reaction



where the helium buffer gas acts as the stabilizing third body. Somewhat surprisingly, the reaction rate was found to be independent of the helium pressure in the range from 0.3 to 1 Torr rather than rising linearly with third-body concentration, as one would expect for a three-body association reaction. The likely explanation for the observed lack of a pressure dependence is that the reaction is an example of a "saturated" three-body reaction, i.e. the lifetime of the collision complex formed in the collision of an NO⁺ ion with DMMP is so long that essentially every collision complex is stabilized at the helium densities used. This is perhaps not too surprising in view of the large number of internal degrees of freedom in a complex containing an organic molecule like DMMP. The rate coefficient measured for reaction (3) is typical of a fast binary ion-molecule reaction and it has been entered as a binary reaction in Table 1. The stability of the NO⁺DMMP cluster suggests that the ionization potential of DMMP exceeds that of NO (9.25 eV), in agreement with the ionization potential of DMMP inferred from electron-impact ionization studies [6].

The reaction of metastable NO⁺ ions with DMMP was investigated only briefly. The rate coefficient and product ion yields were similar to those observed in the case of N₂⁺ ions.

Section IV D

Reactions of H_2O^+ and H_3O^+

H_2O^+ ions were found to react with DMMP by fast dissociative charge transfer. The product branches B_2 , and D were observed. A small product-ion signal was observed at 93 amu (branch B_1), but it could not be unambiguously ascribed to a reaction of H_2O^+ . The dependence of the total rate coefficient and the product yields on ion energy was not investigated in detail since we had some difficulties in separating H_2O^+ and H_3O^+ in the injection mass filter.

The reaction of hydronium ions, H_3O^+ , with DMMP apparently proceeds by proton transfer to DMMP



The product ion at 125 amu was the only product ion of this reaction. The reaction is fast (see Table 1) suggesting that the proton affinity of DMMP is larger than that of H_2O (7.37 eV, [12]). A cursory investigation of the energy dependence of this reaction showed that proton transfer is likely to remain the dominant reaction channel up to ion energies of about 1 eV.

Section IV E

Secondary reactions with DMMP

Secondary reactions of the primary products ions with DMMP were not the principal subject of this study, but some observations made in the course of this work may be of interest. The primary product ions of the dissociative charge transfer reactions, A through D, were found to undergo fast (rate coefficients near $10^{-9} \text{ cm}^3/\text{s}$) reactions with DMMP. An ion of mass 139 amu (possibly DMMPCH_3^+) appears to be by far the most important product of the secondary reactions with DMMP. Further reactions of the 139 amu ion with DMMP appear to be slow.

Section V

Discussion of Results

A detailed discussion of reaction pathways would be rather speculative since the thermochemical information on DMMP is rather limited, the neutral reactions were not determined in this experiment, and the internal energies of the reaction fragments are entirely unknown. There is, however, a fairly close resemblance of the ion-induced product spectra to those observed in electron-impact studies, which is worth discussing in some detail. Several of the reactions appear to proceed by dissociative charge transfer, i.e., one electron from an occupied molecular orbital of the target molecule is transferred to the parent ion with little transfer of translational energy from the ion to internal energy of the target molecule. As a result of the electron transfer, the ionized target molecule may, possibly after intramolecular transfer of energy from electronic to vibrational modes, disintegrate into one or more fragments. Alternatively, it may be collisionally stabilized by colliding with a third particle, or it may be stabilized by emitting a photon. The second two modes of energy disposal tend to be slower than unimolecular decay and will not be considered here. Collisional stabilization may conceivably have an effect in the case where the excess energy is very small and the complex decays rather slowly.

The energy required to remove an electron from the highest occupied orbital which has sufficient energy to cause dissociation into a specified decay channel is the "appearance potential" of the particular ionic fragment. It can be measured by electron impact ionization. It seems plausible that dissociative charge transfer into a particular channel is likely to be exoergic when the parent ion's recombination energy exceeds the appearance potential for that channel. The argument is not entirely cogent, since Franck-Condon limitations in charge transfer and electron impact are not quite equivalent. Also, ion-induced dissociation may proceed by ion-molecule reactions other than charge transfer. In an experiment that only detects charged products, the distinction between dissociative charge transfer and ion-molecule reactions is not always possible.

The appearance potentials of the ions of interest have been measured by electron impact on DMMP [6]. The values for the

product ions in branches A, B₁, B₂, C, D are: A:13.4 eV, B₁: 12.5 eV, B₂: 11.5 eV, C: 13.3 eV, D: 10.48 eV, while the recombination energies of the parent ions are in ascending order: H₃O⁺: 6.23 eV (taken as IP (H) - PA(H₂O)), NO⁺: 9.25 eV, O₂⁺: 12.07 eV, H₂O⁺: 12.61 eV, O⁺: 13.62, N⁺: 14.53, N₂⁺: 15.58 eV, NO⁺ (a³S⁺): 15.7 eV.

Comparison of these values indicates that dissociative charge transfer producing any one of the ions A to C is endoergic for parent ions with recombination energies below 11.5 eV. All branches are exoergic for ions with recombination energies in excess of 13.4 eV, if the transferred electron is captured into the electronic and vibrational ground state of the parent atom or molecule. The experimental data on reactions of the low-energy ions H₃O⁺ and NO⁺ are consistent with expectations. Only proton transfer and clustering occur. No fragmentation of DMMP by dissociative charge transfer or other ion-molecule reactions is observed.

Fragmentation of DMMP via dissociative charge transfer becomes possible energetically in the reaction of O₂⁺. Here, charge transfer is exoergic only for the branches B₂ and D. Consistent with this, our data show that B₂ and D dominate the product yield at thermal energy, however, the endoergic branches A and C occur with smaller yields. The possibility cannot be ruled out that the products A and C are formed through ion-molecule reactions other than charge transfer, i.e., that they may require formation of bonds between O₂ and other product neutrals. The experimental data (see Fig. 1) suggest that, as the O₂⁺ translational energy is increased, branch A (the smallest fragment ion) gains at the expense of D (i.e. DMMP⁺). At the highest translational energies (1.3 eV), the O₂⁺-induced product-ion spectrum is quite similar to that induced by O⁺, which has a 1.55 eV higher recombination energy. This observation suggests that in this case kinetic energy is equally efficient in promoting dissociation as electronic energy. A close collision between the ion and the DMMP molecule with efficient transfer of kinetic to internal energy would be required. In the reaction of H₂O⁺, only branches B₂, B₁, and D can be produced by exoergic charge transfer and only those were observed.

For the remaining ions of higher recombination energies, dissociative charge transfer may be the dominant mechanism for all branches. The experiments showed that, with some minor exceptions, product ion abundances vary little with translational ion energies. This finding is compatible with a mechanism of dissociative charge transfer, in which there is little coupling of translational and internal degrees of freedom. Some minor varia-

tions of product yields with ion energy were observed, most notably in the ratio of branches B_1 and B_2 in the O^+ reaction and in branch D in the N_2^+ reaction. Thus, this simple picture of the reaction mechanism is likely to be incomplete.

A comparison of the product-ion abundances for the reactions of N^+ , N_2^+ , and NO^+ (a^3S^+) indicates that the abundances of the most exoergic branches decrease with increasing recombination energy of the parent ion, while the least exoergic branches become more important. Such observations could perhaps be rationalized by invoking the concept of a random complex (excited DMMP⁺) and considering phase volumes available to different decay modes. In view of the difficulty of justifying complete energy randomization in the complex, we will refrain from such arguments.

The principal motivation for this work was to provide data for model calculations of air discharges containing DMMP and related species with the goal to assess the degree of ion-induced dissociation. In such discharges, H_3C^+ and NO^+ and their hydrates are likely to be the dominant ionic species, but these low-energy ions are not effective in dissociating DMMP. The more energetic ions are effective, but their abundance in air discharges may be small.

Table 1. Total rate coefficients and product-ion yields of ion-molecule reactions with DMMP. The energy ranges given refer to the measurements of total rate coefficients. Product yields are those observed at thermal energy, unless otherwise noted. The abbreviations for product ions are given in the text (Eq. 2).

Ion	Rate coefficient k (10^{-9} cm ³ /s)		Product-ion yield (%)	
O ⁺	1.4	(0.04 to 0.7 eV)	A	60
			B ₁	6
			B ₂	24
			C	10
O ₂ ⁺	0.8	(0.04 to 0.9 eV)	A	18
			B ₂	40
			C	8
			D	34
N ⁺	1.3	(0.04 to 0.9 eV)	A	25
			B ₁	15
			B ₂	30
			C	13
			D	17
N ₂ ⁺	1.1	(0.04 to 1.0 eV)	A	45
			B ₁	18
			C	27
			D	10
NO ⁺	1.1	(0.04 eV)	NO ⁺ •DMMP	100
NO ⁺ (a ³ S ⁺)	~1.0	(0.2 eV)	A	~40 (at 0.2 eV)
			B ₁ + B ₂	~25 (at 0.2 eV)
			C	~20 (at 0.2 eV)
			D	~15 (at 0.2 eV)
H ₂ O ⁺	~ 1.0	(0.04 eV)	A	~0
			B ₂	~66
			C	~ 0
			D	~34
H ₃ O ⁺	~ 1.0	(0.04)	(DMMP) H ⁺	100

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